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Japan Patent

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**NOVEL IMIDAZOLIUM COMPOUND ITS SYNTHESIS METHOD & SYNTHESIS METHOD
OF 2-VINYL -4, 6-DIAMINO-S- TRIAZINE**

[新規イミダゾリュム化合物、該化合物の合成方法及び該化合物から
2-ビニル-4、6-デアミノ-S-トリアジンを合成する方法]

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English Title : Novel imidazolium compound, its synthesis method, & synthesis method of 2-vinyl -4, 6-diamino-s- triazine

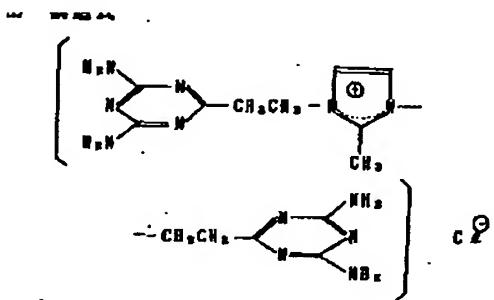
Specification

1. Title of the invention

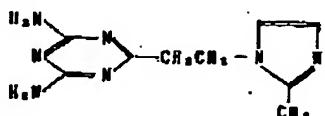
Novel imidazolium compound, its synthesis method, & synthesis method of 2-vinyl -4, 6-diamino-s- triazine

2. Scope of the patent claim

(1) It is 1,3-di- (beta - (4,6'-diamino, -s- triazynil (2')) -ethyl -2-methyl imidazolium chloride represented by the structural formula as follows:



(2) Synthesis method of the compound described in the scope of the patent claim 1 characterized such that 2- [beta - 2'-methylimidazolyl- (D')-ethyl -4,6-damino -s- triazine represented by the structural formula and benzyl chloride are reacted.



(3)) Synthesis method of the compound described in the scope of the patent claim 1 characterized such that structural formula represented by 2- [beta - (2' -methyl imidazolyl -(1')) -ethyl - 4,6-diamino -s- triazine and allyl chloride are reacted in acetic acid.

(4) the synthesis method to synthesized 2-vinyl -4,6-diamino -s-

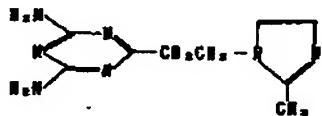
triazine in which the compound described in the scope of the patent claim 1 is reacted with alkali.

3. Detailed explanation of the invention

Present invention relates to the novel imidazolium compound, its synthesis method, & synthesis method of 2-vinyl -4, 6-diamino-s-triazine.

The novel imidazolium compound (hereafter abbreviated as Q salt) obtained by this invention is useful as the precursor substance at the time of synthesizing 2-vinyl 4,6- diamino -a-triazine (hereafter abbreviated as V.T.).

The structural formula of V.T is as follows.



Before explaining the content of present invention in detail, we think it is, first of all, necessary to explain about the usefulness of V.T, its synthesis method and its properties.

It is known that V.T. is useful as a co monomer and when diamino -a- triazine is introduced on the high polymer side chain, the softening point and glass transmission point of the said high polymers rise greatly compared with un-introduced high polymers, and weight increases, solubility changes greatly (for instance, Seo, Kakurai: high polymer dissertation collection, 32, 308 (1975); T.See. K. Abe, H. Homma, T. Kakurai:L Poly Prepn. 20 661(1979)).

Regarding the synthesis of V.T., several methods mentioned below

are known: the method to react biguanide and chloride acrylate (C. G. Overberger et al: J. A.C. A., 80,988 (1958), the method to react dicyan diamide and beta- dimethyl amino - propionitrile (Hoschei Co: Pl. 1.563, 255 (1967), the method to heat 1, 2-di(4',6'- diamino -a-triazinil - ?) cyclo butane to 320 deg C under the decreasing pressure(Asahi Kasei co: Japan Patent disclosure showa 46-35058), the method to heat 2-beta, methoxy ethyl -4.6 -diamino -s- triazine to 350 deg c in the nitrogen gas current (Suddeutsche Kalkstocksoff Weks A.G. Ger Offen, 2,135.8 \$1 (1973) and the like.

Next the properties of V.T will be described.

At m.p. 239~ 241 deg c (W), it is solvable in hot water; difficult to dissolve in heated methanol, heated ethanol, heated acetone; mostly neutral; when dissolved in heated water, and azo bis isobutylonitrile is added, indissolvable polymer is provided into the heated water. TLC (alumina and silica, EtaOH) %Rf=0.0

[illeg]: 3340, 3170, 1680 (forth absorption), 1655 (second absorption), 1550 (first absorption), 1460 (fifth absorption), 1425 (third absorption), 1370, 1265, 1130, 985, 950, 835 (sixth absorption)

NMR (D₆DMSO) : δ6.76 (multiple overlapping lines, 4H), 6.35 ~ 6.45 (3 overlapping lines, 2H); 5.59~5.72 (4 overlapping lines, 1H)

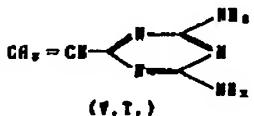
Element analysis values: C% 44.28, H% 5.07, N% 50.62

Regarding each method of aforementioned V.T. synthesis, starting raw materials are expensive sometimes, reaction operations

are sometimes complex, the yields are low, hence making it not suitable for industrial scale manufacturing.

The inventors involved herein studied hard in order to solve the above described problems, as a result, by reacting 2- [beta - 2' -methylimidazolyl- (D') -ethyl -4,6-damino -s- triazine (hereafter abbreviated as 2MA) with benzyl chloride or allyl chloride, said novel imidazolium compound (Q salt) can be obtained with high yield and by reacting said Q salt with alkali, V.T. can be obtained with high yield, they found out.

When these are explained by the reaction formulas, it is as follows:

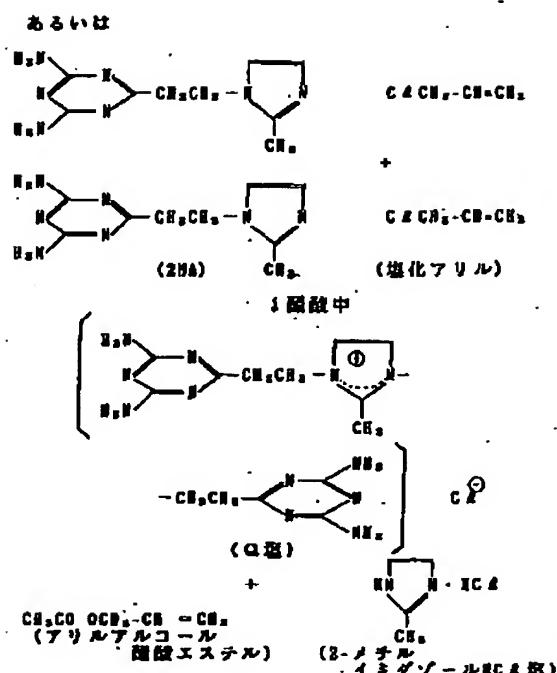
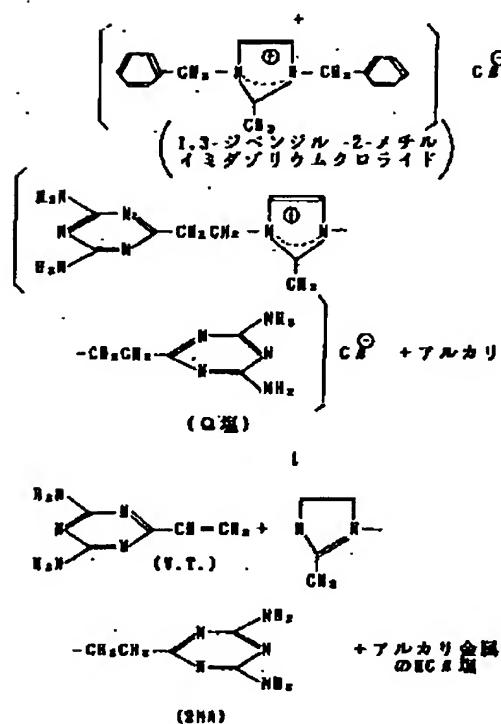
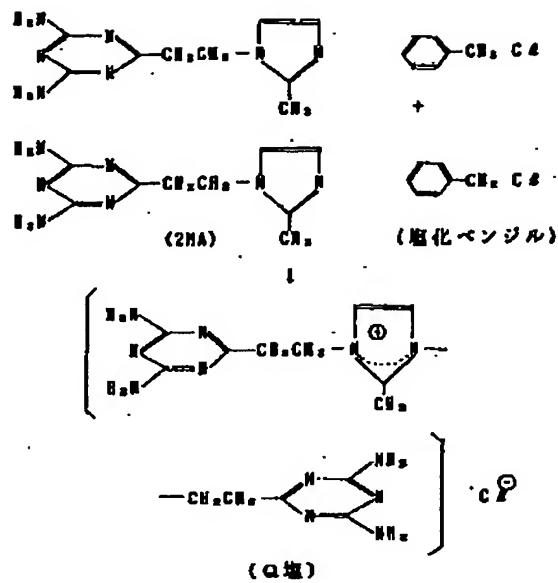


the top half of Bottom right

(Benzyl chloride)

the bottom half of the bottom middle

(Q salt)



First: left side: top to bottom

1,3-dienzyl-2-methyl imidazolium chloride
 +alkali
 (Q salt)

HCl salt of +alkaline salt

Right side: top to bottom

Or

(Allyl chloride)

In acetic acid

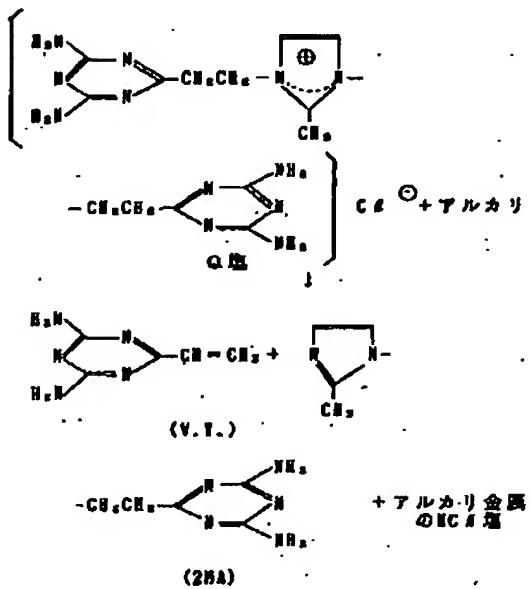
(Q salt)

(Allyl alcohol,

Ester acetate)

(2-methyl

imidazole HCl salt)



Top to bottom

+ alkali

Q salt

HCl salt of +alkaline metal

starting substance 2MA in above described reaction formula is

the compound that can be obtained with high yield using the method described in the Japan Patent disclosure Sho47-36391 gazette from the three parties of aclylonitrile, 2 methyl indazole and dicyan diamide.

The yield of the reaction in which Q salt is formed from 2MA is good, and also, the reaction yield in which V.T. is formed from Q salt is good, the operation of each reactions is simple, so that one can say that the method of present invention is suitable for the execution on the industrial scale.

Next, the embodiments of this reaction will be described.

Raw material system with 4 parties of 2MA, benzyl chloride, suitable amount of sodium sulfide as polymerization preventive agent (Na₂S.9aq) and suitable amount of solvent alcohol are heated and circulated in current for 2 hours while being churned, after which, formation system thus obtained is cooled and targeted rough product (Q salt) is filtered and obtained.

The mole ratio of 2MA and benzyl chloride is 1:1 up to 1:2.0, however, mole ratio 1~1.5 is most preferred. Solvent alcohol amount is, preferably, same weight or more relative to 2MA. As alcohol, methanol, ethanol and isopropanole and the like are suitable.

Other than soda sulfide, various locally sold polymerization preventive agent (for instance, hydroquinone and the like) can be used, but among them, soda sulfide is the most economical.

Refining the targeted rough product is done by recrystallization

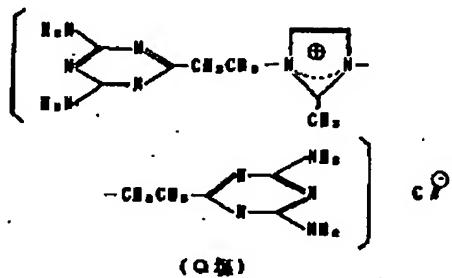
method according to the regular method. As recombination solvent, water or alcohol is used.

Next, other embodiment of present invention will be described.

The raw material system which consists of the four parties of 2MA, allyl chloride, suitable amount of soda sulfide as a polymerization preventive agent ($\text{Na}_2\text{S} \cdot 9\text{aq}$) and suitable amount of acetic acid are, while being churned, heated about 4 hours at 75~93 deg C, the formation system thus obtained is cooled and rough targeted product (Q salt) is filtered and obtained.

The mole ratio of 2MA and allyl chloride is 1:1 up to 1:2.0 but the mole ratio of 1:1.5 is most favorable. The amount of acetic acid is preferably same weight or more relative to 2MA.

The structural formula and the properties of the targeted product thus obtained dare as follows:



(Q salt)

Neutral, colorless crystal, m.p. 230~234 deg C (W), easily dissolve in DMSO or acetic acid, soluble in water, difficult to be dissolved in methanol or ethanol.

[illeg] : 3350 (3rd absorption), 3140 (3rd absorption), 1650 (1st absorption), 1525 (2nd absorption), 1450 (3rd absorption), 1525 (2nd

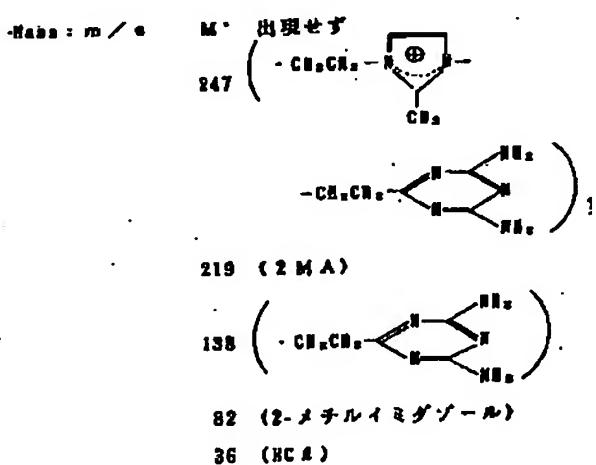
absorption), 1450 (3rd absorption), 1420 (2nd absorption), 1400 (4th absorption), 1330 (8th absorption), 1230 (9th absorption), 1205 (9th absorption), 1165 (7th absorption), 808 (5th absorption), 780 (8th absorption)

NMR (d6-dMSO): δ 7.73. ?2H(imidazole. ? 4, 5th position proton): 6.78.

Br.s.8H (-NH₂): 4.40.m.4H(methylene adjacent to Imidazolium):

2.88.m.4H (methylene adjacent to triazine): 2.64, S.3H) (methyl group)

Mass: m/e M? Does not appear



S2 (2-methyl imidazole)

36 (HCl)

Element analysis:

C% 42.29 (42.80), H% 5.86 (5.39), N% 41.97 (42.78), C e% 8.80 (9.03)

However values in () are theoretical values.

The reaction to synthesize V.T. from Q salt is very easy. the chlorine ions of Q salt is heated a little in alkali and water solvent

of the sufficient amount to neutralize chlorine ions of Q salt, then, difficult-to dissolve V.T is precipitated from the solvent, this is filtered and obtained, and if it is recrystallized, targeted refined product is obtained. As alkali, alkali hydroxide, alkali carbonate, alkali [illeg] and the like are the most suitable.

Next, the result of the testing of present invention will be explained by embodiments.

Embodiment 1

Raw materials system of four parties of 2MA 0.1 mole (21.9g), benzyl chloride 0.2 mole (35.32g), soda sulfide (Na₂S.9aq) 0.002 mole (0.48g), and ethanol 24g are heated and circulated in current for 2 hours while being churned, after which, the formation system thus obtained is cooled and 0.04 mol (18.24g. relative to 2MA yield 96mol %) of targeted raw product (Q salt) is filtered and obtained.

The m.p. of this is 222~225 deg C.

Said targeted rough product is recombined by methanol, furthermore, is recombined by water once again, and identified sample 0.041 mole (16.1 g, vs. 2Mg yield 82 mole %) is obtained

ON the other hand, into the filtered solution at the time of filtering and obtaining the targeted rough product, potassium carbonate water solution is added until the entire pH becomes 12, precipitated crystals is filtered, and is subjected to methanol recombination, the crystals of 0.04 mol at (11.09g vs. 2MS yield 80 mole %) m.p. 209~210 deg C is obtained.

Infrared spectrum of said crystals matched with 1,3, dibenzyl -2-methyl imide zolium chloride of said crystals.

Embodiment 2

The system which consists of three parties of 2MA 0.1mol (21.9g), soda sulfide (Na₂S.9aq) 0.01 mole (2.4g) and acetic acid 30ml is heated to 100 deg C and completely dissolved while being churned, and allyl chloride 0.2 mole (15.3g) is dripped into the system, taking 30 minutes, after which, the internal temperature of 75~93 deg c is maintained for 4 hours. The formation system thus obtained is cooled, 0.037 moles (14.5g vs. 2MA yield rate 74 mole %) the precipitated targeted raw product (Q salt) is obtained. The m.p. of this product is 213 ~ 318 deg C. above described targeted rough product is dissolved in heated water, and a small amount of undissolved product is filtered and separated by heating, and crystals precipitated by cooling from the filtering solutions is filtered and obtained, identified sample 0.03 mole (12.3g, vs. 2MS yield 6 mole %) is obtained. On the other hand, the filtering solution at the time of filtering of the targeted raw product is subjected to filtering under normal pressure, and unreacted allyl chloride 3g and allyl alcohol acetic acid ester 13g were obtained. Furthermore, distillation residue is turned into base by potassium carbonate, using decreased pressure distillation (20mmHg); 2-methyl imidazole of about 2g was recovered.

Embodiment 3

Raw material system consisting of 3 parties of Q salt 0.1 mole (39.25g), water 100 ml and potassium carbonate 0.2 mole (27.6g) were heated and circulated in current for a while and the product thus obtained was cooled, and precipitated crystals were filtered and taken, said crystals were washed by methanol and said crystals were recombined by water once, v.T. 0.084 mole (11.51g vs. Q salt yield 84%) were obtained.

Other heated methanol washing liquid were dried and hardened, and residue were recombined by water, and 2MA 0.078 mole (17.1g vs. Q salt yield 78 mole) were obtained.